PHYSICAL REVIEW B VOLUME 49, NUMBER 6 1 FEBRUARY 1994-II

# Thermodynamics of the one-dimensional six-vertex ferroelectric model with proton tunneling

V. E. Zubkus and V. A. Onischuk
*Institute of Chemical Physics, Russian Academy of Sciences, Kosygina 4, 117977 Moscow, Russia*

E. E. Tornau* and A. Rosengren
*Department of Theoretical Physics, The Royal Institute of Technology, S-100 44 Stockholm, Sweden*
(Received 18 December 1992; revised manuscript received 19 October 1993)

We study a one-dimensional model of ferroelectrics with proton tunneling on the hydrogen bonds. The influence of tunneling on the thermodynamics of the model is considered in the approximation of Nagle [$\exp(-w/T) = 0$] and for energies of the forbidden configurations $w$ much larger than the tunneling constant $\Gamma$. The rearrangement of the energy levels due to the inclusion of proton tunneling is investigated by secular perturbation theory, using $\Gamma/w$ as a small parameter. Exactly solvable six-vertex one-dimensional models with tunneling are obtained as the first nonvanishing orders of this theory. The phase transition from the disordered to the polar phase is found to be first order as in the case of $\Gamma = 0$, but the transition temperature $T_c$ and the entropy jump $\Delta S$ decrease with the increase of the parameter $\delta = \Gamma^2/\varepsilon w$, where $\varepsilon$ is the energy of the excited configurations obeying the ice rule. When $\gamma = (1-\delta) \to 0$, $T_c$, $\Delta S$, and the energy gap, separating the ground ferroelectric state from the excited states, tend to zero as $2\varepsilon/\ln(1/\gamma)$, $(\gamma/2)\ln(1/\gamma)$, and $\varepsilon\gamma$, respectively. The results are compared with the experimental data on the ferroelectric, $K(H_xD_{1-x})PO_4$.

## I. INTRODUCTION

Crystals with a two-minima potential for the protons on the hydrogen (H) bonds at low temperatures undergo phase transitions (PT) induced by ordering of these protons. The nets of H bonds in these crystals may be three dimensional[1] as well as two dimensional[2,3] or one dimensional.[4] Despite this variety, PT in crystals with proton ordering are specified by the same ice rule of Pauling[5,6] which forbids the so-called charged configurations of protons on H bonds at the anion part of the constituent molecule, called a vertex. It means that the strong electrostatic short-range correlations exclude vertices with one, three, and four neighboring protons. The energies of the forbidden configurations, $w$, are much higher than the energies of the configurations allowed by the ice rule. The thermodynamics of these systems is usually investigated by means of exactly solvable six-vertex models which take into account the contributions from the vertices with only two neighboring protons,[2,7] or by approximate cluster methods[8,9] including also the energies of the charged vertices. The nets of H bonds in the exactly solvable six-vertex model ($w \to \infty$) may be either one[10,11] or two dimensional.[7] Whether the low-temperature phase is ferroelectric or antiferroelectric is determined by the choice between the two vertices with the lowest energy. The remaining four vertices have their energies higher by $\varepsilon$ than the lowest-energy vertices. It is known from the exactly solvable two-dimensional six-vertex models[7] that the first-order PT from the disordered high-temperature to the ordered low-temperature phase occurs at the temperature $T = \varepsilon/\ln 2$. A PT does not occur in the one-dimensional model with finite $w$, in contrast to the case of infinite $w$, but the thermodynamic free energy of the system has a sharp anomaly[10,11] in the vicinity of $T = \varepsilon/\ln 2$ causing an anomaly in heat capacity and a finite entropy jump. These results suggest that the main factor determining the PT with proton ordering is rather the ice rule than the dimension of the H-bond net of the considered system.

For real three-dimensional crystals, e.g., the ferroelectrics $KH_2PO_4$ and $PbHPO_4$, tunneling of the protons through a barrier between the two minima is very important, because the tunneling constant $\Gamma$ is of the same order of magnitude as the energies $\varepsilon$ inducing the PT.[4,8,9] Therefore investigation of the influence of proton tunneling on the thermodynamics of the PT should be of great interest. This paper considers this problem for one-dimensional systems.

In Sec. II we formulate the Hamiltonian of our one-dimensional model. Because an exact solution of this model is not known, in Sec. III we develop a secular perturbation theory with a small parameter $\Gamma/w$. The second order of this theory provides us with the secular Hamiltonian for the one-dimensional six-vertex model with tunneling. This Hamiltonian accounts exactly for the influence of proton tunneling on the configurations obeying the ice rule. Finally, we obtain the secular Hamiltonian corresponding to the Nagle model with $\Gamma \neq 0$. In the last section we analyze the influence of tunneling on the PT thermodynamics using the approximation of Nagle, i.e., neglecting all the terms of order of $\exp(-w/T)$.

 

## II. THE HAMILTONIAN

We investigate the one-dimensional chain with $N$ vertices bonded by double H bonds as depicted in Fig. 1. It is assumed that the proton on each of the H bonds is localized either in the left ($L$) or right ($R$) potential well. Correspondingly, the bond can be found in one of the two states shown in Fig. 2. We can also describe the states of the H bond with the localized proton by assigning arrows or Ising spin variables $\sigma^z = \pm 1$ to each of the H bonds. Consequently, the enumeration of proton sites on H bonds (Fig. 2) corresponds to the $4^N$ different arrangements of arrows on the $2N$ bonds.

Let us consider a site with four adjoining H bonds (vertex). Depending on the different arrangements of the protons on the four adjoining H bonds, $2^4$ types of vertices, presented in Fig. 3, can be obtained. These vertices can be divided into seven symmetry classes, hereafter denoted by roman numerals, under the action of the group $G = \{e,\ \sigma_1,\ \sigma_2,\ \sigma_1 \cdot \sigma_2\}$ generated by the reflections $\sigma_1$ and $\sigma_2$ along the vertical and horizontal axes crossing the site. Only six vertices, belonging to classes I, II, and III, obey the ice rule.[5] Our model is based on the following assumptions: (1) the configuration energy of the system, depicted in Fig. 1, is a sum of the configuration energies of all its vertices; (2) the configuration energies of vertices, belonging to the same symmetry class, are equal; (3) the configuration energy of a vertex is the sum of the energies of the protons and vacancies, localized on the adjoining H bonds and coupled with each other by pairwise interactions. These conditions completely determine the Ising Hamiltonian, which describes the energies of system configurations, and has the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \sum_{i=1}^{N} \mathcal{H}_0(i) + \sum_{i=1}^{N} \mathcal{H}_1(i), \tag{1}$$

$$\begin{aligned}\mathcal{H}_0(i) = &-v_1 \left(\sigma^z_{i,1} \cdot \sigma^z_{i+1,1} + \sigma^z_{i,2} \cdot \sigma^z_{i+1,2}\right) \\ &-\frac{1}{2} v_2 \left(\sigma^z_{i,1} \cdot \sigma^z_{i,2} + \sigma^z_{i+1,1} \cdot \sigma^z_{i+1,2}\right) \\ &-v_3 \left(\sigma^z_{i,1} \cdot \sigma^z_{i+1,2} + \sigma^z_{i+1,1} \cdot \sigma^z_{i,2}\right),\end{aligned} \tag{2}$$

$$\mathcal{H}_1(i) = \frac{\Gamma}{2} \left(\sigma^x_{i,1} + \sigma^x_{i,2}\right). \tag{3}$$

Here $\mathcal{H}_0(i)$ is the configuration energy of the vertex formed by a site bonding of $i$th and $(i+1)$th pair of H bonds. The Pauli matrices $\sigma^z_{i,1}$ and $\sigma^z_{i,2}$ depict the localization of protons on the H bond. The $\mathcal{H}_1(i)$ is the energy of the proton tunneling of the $i$th pair of the H bond. According to the enumeration of H bonds by spins, introduced in Fig. 2, the following equations can be obtained:

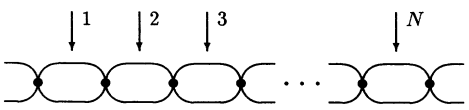


FIG. 1. One-dimensional chain with $N$ vertices bonded by double H bonds.

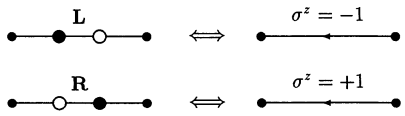


FIG. 2. Two states of a proton on the H bond, corresponding directions of the arrows, and values of the Ising variable.

$$v_1 = -\frac{1}{4}(w_1 + w_3), \quad v_2 = \frac{1}{2}(w_1 + w_2), \quad v_3 = -\frac{1}{4}(w_2 + w_3), \tag{4}$$

which relate the parameters $v_i$ to the configuration energies $w_i$ belonging to symmetry classes I, II, and III, and obeying the ice rule. The configuration energies of the charged classes IV–VII can be expressed as follows:

$$w_4 = w_5 = 0, \quad w_6 = w_7 = -(w_1 + w_2 + w_3). \tag{5}$$

In model (1) the separation of neutral and charged vertices can be performed by introducing the new variables $w$, $\varepsilon_1$, and $\varepsilon_2$ in the following way:

$$\begin{aligned}&w_1 = -w, \quad w_2 = -w + \varepsilon_1, \quad w_3 = -w + \varepsilon_2, \\ &w_4 = w_5 = 0, \quad w_6 = w_7 = 3w - (\varepsilon_1 + \varepsilon_2).\end{aligned} \tag{6}$$

The separation is described by the condition $|\varepsilon_1| \sim |\varepsilon_2| \ll w$. At $w/T \to \infty$ the set of neutral vertices forms an autonomous thermodynamic subsystem. Then only the difference in energies (6) has a physical meaning, and one can choose arbitrarily the value of $w$. Taking $w = \varepsilon_2$, we obtain the parameters of the generalized Nagle model in the form

$$w_1 = -\varepsilon_2, \quad w_2 = \varepsilon_1 - \varepsilon_2, \quad w_3 = 0. \tag{7}$$

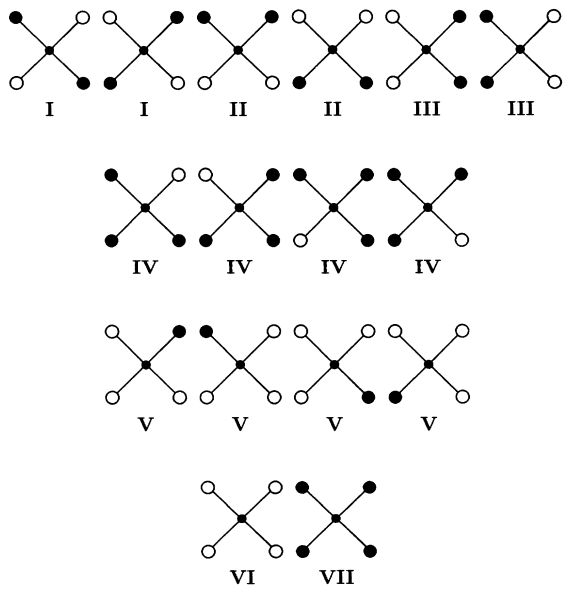


FIG. 3. Sixteen types of the vertices divided into the seven classes of symmetry.

The Nagle model[10] is obtained from (7) at $\varepsilon_1 = 0$ and $\varepsilon_2 = -\varepsilon < 0$. I.e., in that model the vertices of class III have the lowest energy. The first-order PT to the low-temperature ferroelectric phase occurs at $T_c = \varepsilon/\ln 2$. This transition is related to the particular topology of the one-dimensional six-vertex model, i.e., a transition from the ground (ferroelectric) state to any of the excited states cannot occur without the violation of the ice rule by changing the configurations of a finite number of vertices. Consideration of the states with energies of order $w$, violating the ice rule, restores the one-dimensional character of the model and leads to smearing of the PT at $T_c = \varepsilon/\ln 2$. Outside of the approximation of Nagle ($w \gg T_c$) the thermodynamic functions have anomalies[10] in the vicinity of $T_c$, and the terms of order $\exp(-w/T)$ have to be taken into account to describe those anomalies. But at $\exp(-w/T) \sim 0$ the region of the PT shrinks to a point, and the Nagle model roughly describes the anomalies.

Below we investigate the influence of the tunneling on the thermodynamics of the one-dimensional model (1) for the case

$$|\varepsilon_1| \ll w, \quad |\varepsilon_2| \ll w, \quad \Gamma \ll w, \quad \exp(-w/T) \sim 0. \tag{8}$$

The last condition corresponds to the approximation of Nagle in our problem.

## III. THE SECULAR HAMILTONIAN

### A. Zeroth order

If conditions (8) are satisfied, the main contribution to the thermodynamic properties of the system is due to configurations with neutral vertices. In this case proton tunneling leads to a rearrangement of the system of $2+2^N$ eigenvalues of $\mathcal{H}_0$, which is described in terms of secular Hamiltonians.[12] We assume that the Hamiltonian $\mathcal{H}_0$ has the set of quasidegenerate eigenvalues $E_i$ ($i = 1, 2, \ldots, M$), and this set is separated from the other eigenvalues of $\mathcal{H}_0$ by a gap which is considerably larger than the perturbation, described by $\mathcal{H}_1$. In the general case, linear spaces of eigenfunctions of $\mathcal{H}_0$ correspond to each $E_i$. Let us introduce the projection operators on these spaces, $P_i$, and define $P$ and $Q$ as

$$P = \bigoplus_{i=1}^{M} P_i, \quad P \bigoplus Q = 1. \tag{9}$$

Taking into account the terms including the second order of perturbation, the secular Hamiltonian in $P$ space has the form

$$\mathsf{H} = P\mathcal{H}_0 P + P\mathcal{H}_1 P + \mathsf{H}_2,$$
$$\mathsf{H}_2 = \bigoplus_{i=1}^{M} \left[ P\left(\mathcal{H}_1 \frac{Q}{E_i - \mathcal{H}_0}\mathcal{H}_1\right) P_i + P_i\left(\mathcal{H}_1 \frac{Q}{E_i - \mathcal{H}_0}\mathcal{H}_1\right) P \right]. \tag{10}$$

In our case $P$ is the projection operator on the linear space created by the set of $2 + 2^N$ eigenfunctions of $\mathcal{H}_0$ which correspond to the neutral vertices. Then $Q$ projects on the eigenfunctions for which the ice rule is violated at one vertex at least.

The basis of $P$ space consists of the states of the system of neutral vertices. Two states, $L$ and $R$, depicted in Fig. 4(a), are polarized contrary to the remaining, nonpolarized states. These can be distinguished by the two directions of arrows on $N$ pairs of H bonds, as in Fig. 4(b), which may be related to the spin variable $\tau_i^z$ so that the energies of the four vertices in classes I and II are described by the Hamiltonian

$$\mathsf{H}(i) = \frac{1}{2}(w_1 - w_2)\tau_i^z \cdot \tau_{i+1}^z + \frac{1}{2}(w_1 + w_2). \tag{11}$$

Introducing the projection operators $P_R$ and $P_L$, acting on the one-dimensional subspaces $L$ and $R$, and the operator $P_I$, acting on the $2^N$-dimensional space, created by the $N$ pairs of bonds, depicted in Fig. 4, we can describe the projection of $\mathcal{H}_0$ on the $P$ space from (10) as

$$P\mathcal{H}_0 P = N(\varepsilon_2 - w)(P_L \bigoplus P_R) \bigoplus P_I \left[ -\frac{1}{2}\varepsilon_1 \sum_{i=1}^{N} \tau_i^z \cdot \tau_{i+1}^z - N\left(w - \frac{1}{2}\varepsilon_1\right) \right] P_I, \tag{12}$$

where

$$P = P_L \bigoplus P_R \bigoplus P_I. \tag{13}$$

Now we can directly obtain the partition function for $P\mathcal{H}_0 P$ from (12). At $\varepsilon_1 > 0$ we have

$$\mathcal{Z}_N^{(0)} = \exp\left(\frac{N(w - \varepsilon_2)}{T}\right)\left\{2 + \exp\left(\frac{N\varepsilon_2}{T}\right)\left[1 + \exp\left(-\frac{\varepsilon_1}{T}\right)\right]^N\right\}. \tag{14}$$

It is evident from (12) that the energy $N\psi$, where

$$\psi = \begin{cases} -\varepsilon_2, & \varepsilon_1 > 0, \\ \varepsilon_1 - \varepsilon_2, & \varepsilon_1 < 0, \end{cases} \tag{15}$$

when $\psi > 0$, is the width of the gap between the low-energy ordered states $L$ and $R$, and the $2^N$ disordered states of the $P_I$ space. If the gap does exist, i.e., $\psi > 0$, then the equation

$$\exp\left(-\frac{\varepsilon_2}{T}\right) = 1 + \exp\left(-\frac{\varepsilon_1}{T}\right)$$

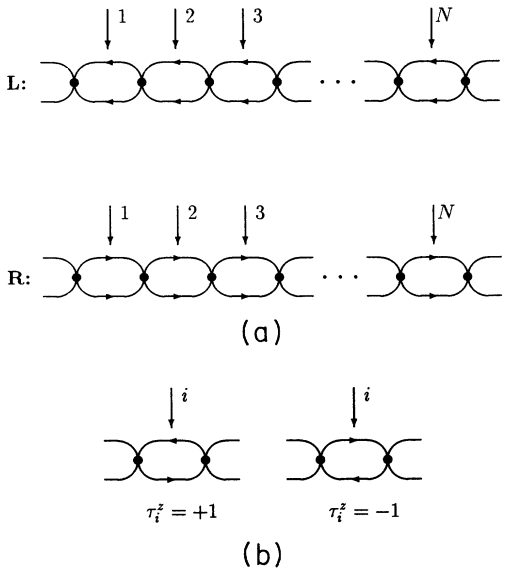


FIG. 4. Polarized states of a system of the neutral vertices (a) and corresponding eigenvalues of the spin operators $\tau_i^z$ (b).

has a unique solution $T_c$. At $\varepsilon_1 = 0$ and $\varepsilon_2 = -\varepsilon < 0$, we obtain the result of Nagle[10] $T_c = \varepsilon/\ln 2$. The first cause of the PT is the macroscopic nature of the gap $N\psi$ and the exponential number ($2^N$ in the case of Nagle) of disordered states above this gap. The second cause is related to the approximation of Nagle, for which all charged excited states of $Q$ space with excitation energies of the order of $w$ are neglected. It is those states, located inside the gap, that smear the PT.

The complete linear space of $\mathcal{H}_0 + \mathcal{H}_1$ has as its basis the eigenfunctions of $\mathcal{H}_0$, which correspond to the $4^N$ arrangements of arrows on the H bonds (see Fig. 1). Let $\psi_\sigma$ be the eigenfunctions of $\hat{S}^z$, corresponding to spin 1/2: $\hat{S}^z\psi_\sigma = (\sigma/2)\psi_\sigma$, $\sigma = \pm 1$. Then there is a one-to-one correspondence between each pair of H bonds and the vectors

$$\psi(\hat{\sigma}) = \begin{pmatrix} \psi_{\sigma_1} \\ \psi_{\sigma_2} \end{pmatrix}, \quad \bar{\sigma} = \begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix}. \tag{16}$$

The vectors $\psi(\hat{\sigma})$ form a basis of a complex four-dimensional linear space. Each of the $4^N$ arrangements of arrows on the H bonds is described by a set $(\bar{\sigma}_1, \bar{\sigma}_2, \ldots, \bar{\sigma}_N)$. Every member of this set is in a one-to-one correspondence with a function

$$\phi(\hat{\sigma}_1, \hat{\sigma}_2, \ldots, \hat{\sigma}_N) = \bigotimes_{i=1}^{N} \psi(\hat{\sigma}_i). \tag{17}$$

These functions are the eigenfunctions of $\mathcal{H}_0$. They form an orthogonal basis of a $4^N$-dimensional complex linear space for all the operators considered. For example, the configurations $L$ and $R$ correspond to the functions of the basis (17) of the form

$$\phi_L = \bigotimes_{i=1}^{N} \psi(-\hat{1}_i), \quad \phi_R = \bigotimes_{i=1}^{N} \psi(\hat{1}_i), \quad \hat{1} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \tag{18}$$

$$-\hat{1} = \begin{pmatrix} -1 \\ -1 \end{pmatrix}.$$

Let us define the operators $\tilde{S}_\tau^\pm$ ($\tau = \pm 1$) acting on the four-dimensional linear space of the functions (16)

$$\tilde{S}_1^\pm = \begin{pmatrix} 1 \\ S^\pm \end{pmatrix}, \quad \tilde{S}_{-1}^\pm = \begin{pmatrix} S^\pm \\ 1 \end{pmatrix}, \tag{19}$$

where $S^\pm$ are the spin-flip operators in the two-dimensional space of spinors $\psi_\sigma$. Using (19), we define the operators $\tilde{S}_{i,\tau}^\pm$ that change the direction of arrows from left to right and vice versa [see Fig. 5(a), where the index $i = 1, 2, \ldots, N$ is omitted for simplicity]. The index $\tau = \pm 1$ is the eigenvalue of the Pauli matrix $\tau^z$ corresponding to the particular direction of arrows [see Fig. 4(b)]. Now all the $2^N$ basis functions (17), which belong to the excited configurations obeying the ice rule, can be written in terms of $\tilde{S}_{i,\tau}^\pm$ acting on $\phi_L$. The perturbation operator $\mathcal{H}_1$ (3) can be expressed as

$$\mathcal{H}_1 = \frac{\Gamma}{2} \sum_{i=1}^{N} \sum_{\tau=\pm 1} \left( \tilde{S}_{i,\tau}^+ + \tilde{S}_{i,\tau}^- \right). \tag{20}$$

It follows from Fig. 5(a) that $\mathcal{H}_1$, acting on each of the

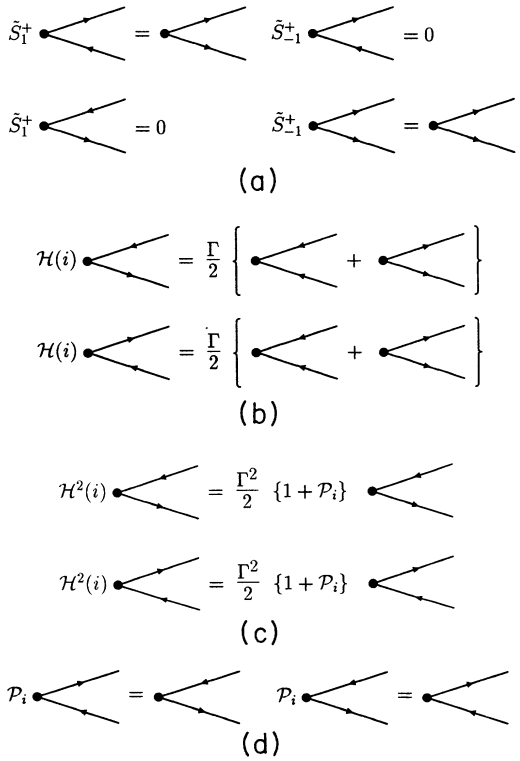


FIG. 5. Action of the operators (a) $\tilde{S}_\tau^+$, (b) $\mathcal{H}(i)$, (c) $\mathcal{H}^2(i)$, and (d) $\mathcal{P}_i$ on the direction of an arrow.

$2 + 2^N$ functions of the $P$ space, transforms them either to zero or to functions of the $Q$ space. As a consequence,

$$\mathsf{H}_1 \equiv P\mathcal{H}_1 P = 0. \tag{21}$$

### B. Second order

To calculate $\mathsf{H}_2$ (10), we use expansion (13) and basis (17) in the $2^N$-dimensional $P_I$ subspace. Now only the sum of the diagonal terms

$$\mathsf{H}_2 = P_I \mathsf{H}_2 P_I \bigoplus H_L \left(P_L \bigoplus P_R\right) \tag{22}$$

is not equal to zero. We took into account in (22) that $P_L \mathsf{H}_2 P_L = H_L P_L$, $P_R \mathsf{H}_2 P_R = H_R P_R$, and $H_L = H_R$ due to the one-dimensionality of $P_L$ and $P_R$. Then, for $\varepsilon_1 > 0$,

$$P_I \mathsf{H}_2 P_I = -\frac{2}{w} P_I \left(\mathcal{H}_1 Q \mathcal{H}_1\right) P_I = -\frac{2}{w} \sum_{i=1}^{N} P_I \mathcal{H}^2(i) P_I. \tag{23}$$

In deriving (23) the relations $\mathcal{H}_1(i) Q \mathcal{H}_1(j) = 0$, for $i \neq j$, and $P_I \left(\mathcal{H}_1 Q \mathcal{H}_1\right) P_I = P_I \mathcal{H}_1^2 P_I$, as well as the condition $\varepsilon_1 \ll w$, were taken into account. The action of

$$\mathcal{H}(i) = \frac{\Gamma}{2} \sum_{\tau=\pm 1} \left(\tilde{S}^{+}_{i,\tau} + \tilde{S}^{-}_{i,\tau}\right)$$

on the $P_I$ states can be depicted as a flipping of the arrows which correspond to the $i$th pair of the H bond [see Figs. 5(b)–5(d)], where $\mathcal{P}_i$ is the spin-flip operator. $\mathcal{P}_i$ can be expressed in terms of the Pauli matrices as $\mathcal{P}_i = \tau_i^x$. Using Fig. 5(c), Eq. (23) is rewritten as

$$P_I \mathsf{H}_2 P_I = -\frac{\Gamma^2}{w} \sum_{i=1}^{N} \left(\tau_i^x + 1\right). \tag{24}$$

From the definition of $H_L$ and (10) we obtain

$$H_L = \langle \phi_L | \mathsf{H}_2 | \phi_L \rangle = -N \frac{\Gamma^2}{w}.$$

Substitution of (24) into (22) leads to the expression

$$\mathsf{H}_2 = -N \frac{\Gamma^2}{w} \left[P_I \left(\frac{1}{N} \sum_{i=1}^{N} \tau_i^x + 1\right) P_I \bigoplus \left(P_R \bigoplus P_L\right)\right]. \tag{25}$$

Assembling (12), (21), and (25), we obtain the secular Hamiltonian in the form

$$\begin{aligned} \mathsf{H} &= \mathsf{H}_0 + \mathsf{H}_1 + \mathsf{H}_2 \\ &= P_I \left[-\frac{1}{2}\varepsilon_1 \sum_{i=1}^{N} \tau_i^z \cdot \tau_{i+1}^z - \frac{\Gamma^2}{w} \sum_{i=1}^{N} \tau_i^x - N\left(\varepsilon_2 - \frac{1}{2}\varepsilon_1\right)\right] P_I \bigoplus 0 \cdot \left(P_R \bigoplus P_L\right) - N\left[\frac{\Gamma^2}{w} + w - \varepsilon_2\right] P. \end{aligned} \tag{26}$$

The last term in (26), proportional to $P$, defines the position of the $P$ levels. The second bracket of the direct sum is related to the polarized states $\phi_L$ and $\phi_R$, which do not mix with those of $P_I$ type. Nevertheless, the energy gap between $\phi_L$, $\phi_R$, and $P_I$ states changes due to the tunneling. To analyze this effect, we consider the particular case of this model at $\varepsilon_1 = 0$, $\varepsilon_2 = -\varepsilon < 0$, and $\Gamma \neq 0$. Then the secular Hamiltonian (26) has the form

$$\mathsf{H}_{\mathcal{N}} = P_I \left[-\frac{\Gamma^2}{w} \sum_{i=1}^{N} \tau_i^x + N\varepsilon\right] P_I \bigoplus 0 \cdot \left(P_R \bigoplus P_L\right) - N\left[\frac{\Gamma^2}{w} + w + \varepsilon\right] P. \tag{27}$$

The lower boundary of the energy spectrum of the first term corresponds to $\tau_i^x = +1$ and is equal (per site) to the value of the energy gap between the $\phi_L$, $\phi_R$, and the $P_I$ states

$$\psi = \varepsilon(1 - \delta), \tag{28}$$

where $\delta = \Gamma^2/\varepsilon w$. The gap decreases with increasing $\Gamma$ and disappears at $\delta = 1$. The same is true for $\varepsilon_1 \neq 0$.

## IV. THE NAGLE MODEL WITH TUNNELING

All contributions of the $Q$ states to the partition function are neglected in the approximation of Nagle [$\exp(-w/T) = 0$]. The thermodynamics is defined by the secular Hamiltonian (26). We consider two cases of the Nagle model with tunneling ($\varepsilon_2 = -\varepsilon < 0$, $\Gamma \neq 0$), those with $\varepsilon_1 = 0$ and $\varepsilon_1 > 0$.

### A. $\varepsilon_1 = 0$

The partition function for the Hamiltonian (27) is expressed as

$$\mathcal{Z}_{\mathcal{N}} = 2 + f(z)^N, \quad f(z) = 2\exp(-z)\cosh(\delta z), \tag{29}$$

where $z = \varepsilon/T$. The thermodynamic behavior differs in the regions with $(0 \leq \delta < 1)$ or without $(1 \leq \delta < \infty)$ a gap (28). In the first case, the function $f(z)$ decreases monotonically from $f(0) = 2$ to $f(\infty) = 0$. Therefore the equation $f(z) = 1$ has a unique solution $z_c = \varepsilon/T_c$. The free energy per site is

$$\varphi(T) = \begin{cases} -(T/N)\ln 2, & T < T_c, \\ -T\ln f(z), & T > T_c. \end{cases} \quad (30)$$

At $T = T_c$, a first-order PT occurs with the entropy jump (per site) $\Delta S = z_c[1 - \delta\tanh(\delta z_c)]$. An increase of the tunneling parameter $\Gamma$ leads to a decrease of the gap (28) and of the transition temperature $T_c$. When $\gamma = (1-\delta) \to 0$, the temperature $T_c$ and the entropy jump $\Delta S$ tend to zero as $2\varepsilon/\ln(1/\gamma)$ and $(\gamma/2)\ln(1/\gamma)$, respectively.

In the case with no gap, we obtain $f(z) > \exp[-z(1-\delta)]$ in the interval $0 \le z < \infty$. Then the equation $f(z) = 1$ has no solutions, and the main contribution to the partition function is given by the second term of (29). The thermodynamics is determined by the behavior of free Ising spins in the field $h = \Gamma^2/w = \delta\varepsilon$. In this case the tunneling completely destroys the singular behavior of the thermodynamic functions characteristic of the Nagle model with $\Gamma = 0$.

### B. $\varepsilon_1 > 0$

The partition function for the Hamiltonian (26) has the form

$$\mathcal{Z} = 2 + \exp\left[\frac{N}{T}\left(\varepsilon_2 - \frac{1}{2}\varepsilon_1\right)\right]\mathcal{Z}_h, \quad (31)$$

where $\mathcal{Z}_h$ is the partition function of the one-dimensional Ising model[13] in a transverse field $h$ with the Hamiltonian

$$\mathsf{H}_h = -J\sum_{i=1}^{N}\tau_i^z\cdot\tau_{i+1}^z - h\sum_{i=1}^{N}\tau_i^x, \quad (32)$$

where $J = \varepsilon_1/2$ and $h = \Gamma^2/w$. The Hamiltonian (32) was diagonalized by Lieb *et al.*[14] The partition function is

$$\mathcal{Z}_h = \exp\left(-\frac{N\varphi_h(T)}{T}\right), \quad (33)$$

where

$$\varphi_h(T) = -\int_{-\pi}^{\pi}\frac{dq}{2\pi}\varepsilon(q) - T\int_{-\pi}^{\pi}\frac{dq}{2\pi}\ln\left[1+\exp\left(-\frac{2\varepsilon(q)}{T}\right)\right], \quad (34)$$

is the free energy per spin, and $\varepsilon(q) = \sqrt{J^2 + 2Jh\cos q + h^2}$. Substitution of (33) into (31) yields

$$\mathcal{Z} = 2 + \exp\left(-\frac{N\psi(T)}{T}\right),$$
$$\psi(T) = \frac{1}{2}\varepsilon_1 - \varepsilon_2 + \varphi_h(T). \quad (35)$$

The thermodynamic behavior of the Nagle model with tunneling is determined by the behavior of the free energy of this model at zero temperature

$$\psi(0) = \frac{1}{2}\varepsilon_1 - \varepsilon_2 - \int_{-\pi}^{\pi}\frac{dq}{2\pi}\varepsilon(q). \quad (36)$$

A comparison of (36) to (26) shows that

$$N\psi(0) > 0 \quad (37)$$

is the energy gap. Therefore, the inequality (37) is the condition of existence for the gap. For $\varepsilon_1 = 0$, $\varepsilon_2 = -\varepsilon < 0$, $h = \Gamma^2/w$, we get expression (28) from (36) directly.

Consider the thermodynamics of the system when condition (37) is valid. It follows from (35) that, with the decrease of $T$ from infinity to zero, the function $\psi(T)$ increases monotonously from $\psi(\infty) = -\infty$ to $\psi(0) > 0$. Thus, if condition (37) is valid, the equation $\psi(T) = 0$ has a unique solution $T_c \neq 0$, where $T_c$ is the temperature of the first-order PT. The free energy per site has the form

$$\varphi(T) = -(T/N)\ln\mathcal{Z} = \begin{cases} -(T/N)\ln 2, & T < T_c, \\ \psi(T), & T > T_c. \end{cases} \quad (38)$$

The entropy jump is expressed as

$$\Delta S = \int_{-\pi}^{\pi}\frac{dq}{2\pi}\ln\left[1+\exp\left(-\frac{2\varepsilon(q)}{T_c}\right)\right] + T_c\int_{-\pi}^{\pi}\frac{dq}{2\pi}\left\{1-\tanh\left(\frac{\varepsilon(q)}{T_c}\right)\right\}. \quad (39)$$

When the energy gap (36) disappears ($\psi(0) \le 0$), then the free energy per site is $\varphi(T) = \psi(T)$. Because $\psi(T)$ is an analytic function of $T$, the thermodynamic functions have no singularities.

Let us investigate the influence of $\Gamma$ on the behavior of $T_c$ and $\psi(0)$ at $\varepsilon_1 > 0$. From (34) and (35) we obtain

$$\psi(0) = \varepsilon - \frac{1}{2}\varepsilon_1\int_{-\pi}^{\pi}\frac{dq}{2\pi}\left(\sqrt{1+2x\cos q + x^2} - 1\right),$$

$$x = \frac{2\Gamma^2}{\varepsilon_1 w} > 0.$$

I.e., with the increase of $x$ from zero to infinity, the free energy $\psi(0)$ decreases monotonously from $\varepsilon$ to $-\infty$. Therefore the equation $\psi(0) = 0$ has the unique solution $x_0 = x_0(y)$, where $y = \varepsilon_1/2\varepsilon$, which defines the critical value of the tunneling constant $\Gamma_0^2(y) = \varepsilon w y x_0(y)$. The energy gap $N\psi(0)$ vanishes at $\Gamma = \Gamma_0(y)$. The dependence of $\delta_0 = \Gamma_0^2(y)/\varepsilon w$ on $y$ is depicted in Fig. 6. In Fig. 7 the dependence of $T_c$ on $\delta$ is shown, together with the cluster approximation results for $K(H_xD_{1-x})PO_4$ crystals.[8,9]

## V. CONCLUSIONS

In the approximation of Nagle [$\exp(-w/T) = 0$] only the thermodynamic contribution from the $2 + 2^N$ states, for which the ice rule is valid, is taken into account. Of these states, $2^N$ states are related to the disordered phase

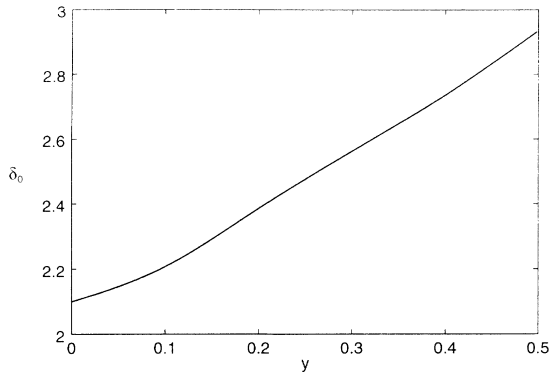


FIG. 6. Dependence of $\delta_0 = \Gamma_0^2/\varepsilon w$ on $y = \varepsilon_1/2\varepsilon$.

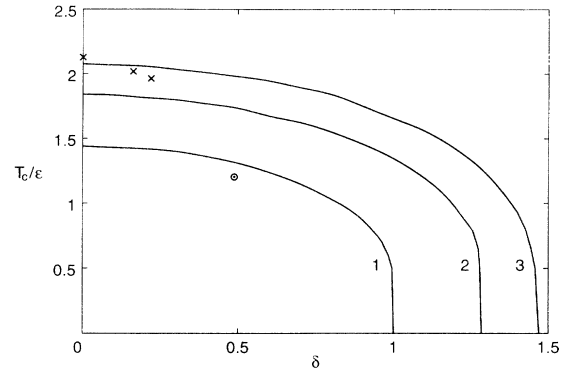


FIG. 7. Dependences of $T_c/\varepsilon$ on $\delta = \Gamma^2/\varepsilon w$ in the interval $0 \leq \delta \leq \delta_0(y)$ at $y = \varepsilon_1/2\varepsilon = 0$ (curve 1), 0.2 (2), and 0.5 (3). Crosses correspond to the cluster approximation fitted to the experimental data on $KH_2PO_4$ and $KD_2PO_4$ crystals. The circled dot corresponds to the values used for $KH_2PO_4$: $T_c = 120$ K, $\varepsilon = 100$ K, $w = 800$ K, and $\Gamma = 2\varepsilon = 200$ K (Refs. 8 and 9).

of the proton system and separated from the two polarized states by an energy gap proportional to $N$. This gap $N\psi(0)$ induces the first-order PT in the approximation of Nagle. The PT is smeared due to the contribution of the numerous states, violating the ice rule, whose energies are inside the gap. At $\exp(-w/T) \ll 1$, the smearing occurs in the very vicinity of $T_c$,[10] and the thermodynamic functions have anomalies roughly approximated by the first-order PT at $T_c$. Thus, the $2 + 2^N$ neutral states give the main contribution to the thermodynamics of the model in this case. We have investigated the influence of proton tunneling on the thermodynamics of the neutral states assuming that $\Gamma/w \ll 1$, $|\varepsilon_1|/w \ll 1$, and $|\varepsilon_2|/w \ll 1$, where $\varepsilon_1$ and $\varepsilon_2$ correspond to the excitation energies of the neutral configurations. The main result at $\varepsilon_1 = 0$, $\varepsilon_2 = -\varepsilon$ is that the energy gap vanishes at the particular value of the tunneling constant $\Gamma_0 = \sqrt{\varepsilon w}$. The thermodynamics of the model at $\varepsilon_1 > 0$ depends on two parameters $\delta = \Gamma^2/\varepsilon w$ and $y = \varepsilon_1/2\varepsilon$. The dependence of $T_c$ and the energy gap on $\Gamma$ are analogous to those in the case $\varepsilon_1 = 0$. The decrease of the PT temperature $T_c$ and the entropy jump $\Delta S$ with the increase of the tunneling constant $\Gamma$ is in qualitative agreement with the data for $K(H_xD_{1-x})PO_4$.[8,9]

## ACKNOWLEDGMENTS

V.A.O. expresses his gratitude to the company "ELORMA" and the Russian Fund of Fundamental Research (Project No. 93-03-18540). E.E.T. thanks the Swedish Institute, and A.R. the Swedish Natural Science Research Council for financial support. We also acknowledge the assistance of G. Grigelionis.

* Permanent address: Semiconductor Physics Institute, Goštauto 11, 2600 Vilnius, Lithuania.

[1] R. J. Nelmes, J. M. Meyer, and J. E. Tibballs, J. Phys. C **15**, 59 (1982).

[2] S. R. Salinas and J. F. Nagle, Phys. Rev. B **9**, 4920 (1974); R. Youngblood and J. K. Kjems, *ibid.* **20**, 3792 (1979).

[3] G. R. Allen, J. Chem. Phys. **60**, 3299 (1974).

[4] A. Lopez-Echarri, M. J. Tello, and M. A. P. Jubindo, Solid State Commun. **38**, 383 (1981).

[5] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1938).

[6] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[7] E. H. Lieb and F. Y. Wu, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, New York, 1971), Vol. 1, p. 332.

[8] R. Blinc and B. Zeks, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[9] V. G. Vaks, N. E. Zein, and B. A. Strukov, Phys. Status Solidi A **30**, 801 (1975).

[10] J. F. Nagle, Am. J. Phys. **36**, 1114 (1968).

[11] L. C. Menezes and S. R. Salinas, Nuovo Cimento B **39**, 105 (1977).

[12] L. N. Bulayevsky, Zh. Eksp. Teor. Fiz. **51**, 230 (1966) [Sov. Phys. JETP **24**, 154 (1967)].

[13] D. C. Mattis, *Theory of Magnetism* (Springer, Berlin, 1985), Vol. 2.

[14] E. H. Lieb, T. Schultz, and D. Mattis, Ann. Phys. **16**, 407 (1961).